High-pressure Raman study of the Sr_2CaWO_6 double perovskite

High-pressure Raman study of the Sr_2CaWO_6 double perovskite

B Manoun[1,3]**, J M Igartua**[2]**, M Gateshki**[2] **and S K Saxena**[1]

[1] Center for Study of Matter at Extreme Conditions (CeSMEC), Florida International University, VH-140, University Park, Miami, FL 33199, USA
[2] Fisika Aplikatua II Saila, Zientzia eta Teknologia Fakultatea, Euskal Herriko Unibertsitatea, PO Box 644, Bilbao 48080, Spain

E-mail: manounb@fiu.edu

Abstract
An *in situ* Raman spectroscopic study was conducted to explore the pressure-induced phase transformation of Sr_2CaWO_6 to pressures of 50.8 GPa and room temperature. Group theory yields 24 Raman active modes for Sr_2CaWO_6, of which 17 are observed at ambient conditions. Upon elevation of pressure to 3.2 GPa, the results suggest some structural changes, possibly a phase transition. At 10.4 GPa, new modes at high frequencies (824 and 903 cm^{-1}) come into existence. As the material is compressed further, the intensities of the bands, especially the W–O stretching modes, observed at 824 and 903 cm^{-1} become stronger, while those centred at 863 and 937 cm^{-1} (at 10.4 GPa) decrease significantly, until disappearance. These changes in the spectrum indicate clearly that Sr_2CaWO_6 undergoes a phase transition at 9.7 ± 0.7 GPa. Upon release of pressure to ambient conditions, a new phase is observed with ten bands compared to the 17 observed in the original phase.

1. Introduction

In recent years, compounds with the general formula $A_2BB'O_6$ and double-perovskite structure have been extensively studied. This attention is due to the fact that many compounds of this family present interesting electrical and magnetic properties that could be used in technological applications [1, 2]. For instance, these types of materials are promising candidates for future spin based electronics. Depending on their valences and relative radii, transition metals often occupy the B-site, which can accommodate two different metal ions. When, in a material, one spin channel is metallic and another spin channel is insulating, the material is termed half-metallic (HM). Due to the high order of spin polarization, some of the double perovskites

---

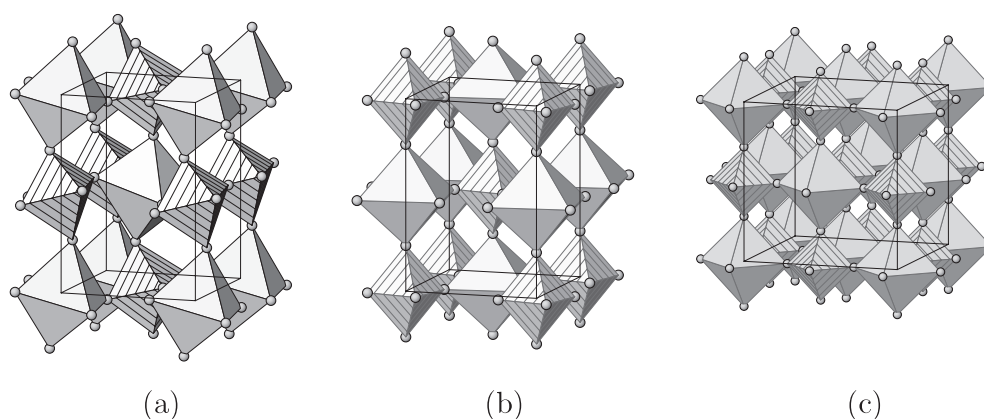[3] Author to whom any correspondence should be addressed.

Figure 1. Ordered perovskite structure models for the different phases of Sr_2CaWO_6: (a) $P2_1/n$, (b) $I4/m$ and (c) $Fm\bar{3}m$.

show very good HM characteristics. Ferromagnetism and half-metallicity, with a high spin polarization at the Fermi level, make them promising for spin devices.

In a recent publication [3] the structure of the ordered double perovskite oxide Sr_2CaWO_6, obtained by conventional x-ray diffraction measurements of powder samples, has been reported: it has the $P2_1/n$ symmetry, at room temperature. As temperature is increased, the compound shows two phase transitions, which change the symmetry from monoclinic to tetragonal ($I4/m$) at 1130 K, and then to cubic ($Fm\bar{3}m$) at 1250 K. Figure 1 shows the ordered perovskite structure models for the three symmetries. As it is known, and can be seen in figure 1, the double-perovskite structure can be represented as a three-dimensional network of alternating CaO_6 and WO_6 octahedra, with Sr atoms occupying the interstitial spaces.

To our knowledge, Raman studies on these double perovskites have been few [4, 5]. Raman spectroscopy has not been a usual technique for double-perovskite analysis. Also, as far as we know, this is the first time that these materials have been investigated at high pressure. We plan to do a systematic analysis, by Raman spectroscopy at room pressure and at high pressures, of some perovskites in the Sr_2CaWO_6 family, starting with this work. The investigation of the double perovskite Sr_2CaWO_6 by Raman spectroscopy at high pressure will characterize this material (at room temperature and high pressure), and will allow us to see whether Sr_2CaWO_6 transforms upon increasing (and decreasing) pressure. Another important point is to evaluate the grade of reversibility of the possible high pressure induced phase transitions present in the compound.

2. Experimental details

2.1. Sample preparation

For the preparation of the samples, the standard method of solid state chemical reaction has been used. Stoichiometric amounts of the reacting compounds were mixed according to the following chemical reaction:

$$2SrCO_3 + CaCO_3 + WO_3 \rightarrow Sr_2CaWO_6 + 3CO_2\uparrow.$$
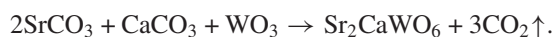
The reacting compounds (all delivered by Sigma-Aldrich) had the following purities: $SrCO_3$(99.995%), WO_3(99.995%) and $CaCO_3$(99.995%). All compounds were used as received, with the exception of $CaCO_3$, which was heated at 420 K for 12 h, before starting the

synthesis procedure. The starting materials were mixed and ground in an agate mortar; and heated in air in alumina crucibles. The following heat treatment was used: 24 h at 1170 K; 24 h at 1270 K; and 48 h at 1370 K. After each heating, the samples were cooled down slowly (3 K min^{-1}); and ground to improve the homogeneity. In order to control the quality of the obtained materials, x-ray diffraction measurements were performed after each heating.

2.2. Raman spectroscopy

Raman spectra were measured in a back-scattering arrangement, on compression and on decompression. Raman spectra were collected at room temperature and room pressure by using a high-throughput holographic imaging spectrograph with a volume transmission grating, holographic notch filter and thermoelectrically cooled CCD detector (Physics Spectra), with the resolution of 4 cm^{-1}. The spectrometer was regularly calibrated by using the neon lines. A Ti^{3+} sapphire laser pumped by an argon ion laser was tuned at 785 nm. The laser power was operated at 220 mW at pressures to 29 GPa; and 310 mW at high pressures. The incident laser beam was focused with the spot size of 5 μm by the objective (+20) to excite the sample. The spectrometer and the Raman spectra were calibrated using the Raman modes of diamond and sulfur, as well as of the neon emission spectrum. The exposure time was 7 min with two accumulations. High-pressure Raman measurements were conducted at room temperature by using a gasketed high-pressure diamond anvil cell (DAC). The sample was placed in a 400 μm steel gasket hole 68 μm in initial thickness and 150 μm in diameter. Ruby chips were loaded with the sample at various spots as pressure markers. Pressures were determined by using the pressure-dependent spectral shift of the sharp ruby fluorescence R1 line shift [6], excited by an argon ion laser with the wavelength of 514.5 nm. The focused laser spot on the sample was close to the ruby chip, so the pressure difference will be small.

3. Results and discussion

Figure 2 shows the Raman spectrum of Sr_2CaWO_6 recorded at ambient conditions.

According to the factor group analysis [7], 24 Raman active modes, represented as $M = 12A_g + 12B_g$, should be observed for the $P2_1/n$ structure of Sr_2CaWO_6 in the Raman experiment. However, the number of observed modes is 17 (as marked in the figure): significantly smaller than expected. This may be attributed to accidental degeneracy of a number of modes. Moreover, some weak bands are most likely overlapped by much stronger bands.

Since the Sr_2CaWO_6 specimen is a polycrystalline powder, we cannot precisely assign the observed modes using a combination of the single-crystal orientation and the polarized Raman scattering. However, the observed Raman modes can be classified into three general families of lattice vibrations: Sr–O external modes, as well as translational and rotational modes of the WO_6 octahedra, at frequencies below 200 cm^{-1}; O–W–O bending vibrations, in the 200–500 cm^{-1} region; and W–O stretching modes, at frequencies over 500 cm^{-1}. These frequency families were also observed in many tungsten oxides such as WO_3 [8], ABW_3O_9 [9]; and in double perovskites, such as Ba_2MWO_6 and Ba_2MMoO_6 (M = Ni, Co, Mg, Zn, Cd, Ca) [4] and in Pb_2MgWO_6 [5]. For a regular WO_6 octahedron the valence for every W–O bond is equal to 1. In the W–O–W contact, the W–O bonds contribute to the valence of oxygen (1 + 1 = 2). The replacement of the W atom by Ca, with lower valence, will lead to a shortening of some of the W–O bonds. The W–O bonds give rise to bands at high frequencies. Therefore, we may assign, unambiguously, the relatively sharp band at 921.6 cm^{-1}, and the shoulder around 899 cm^{-1}, to the W–O stretching vibrations. Such modes are frequently observed in tungsten
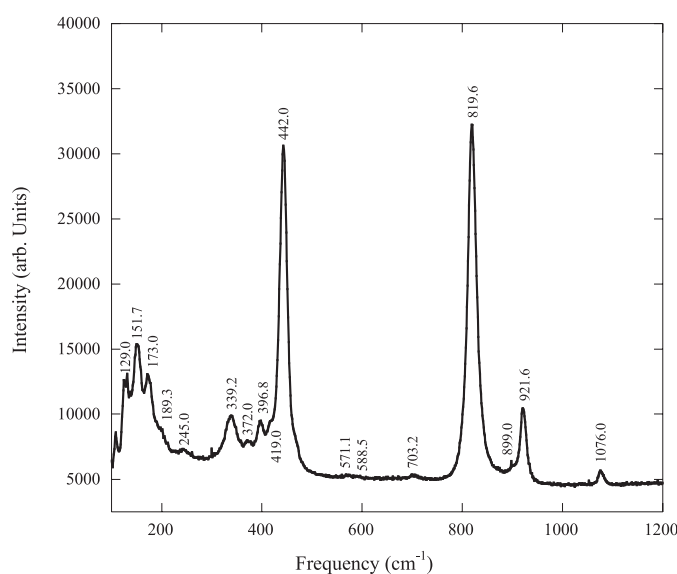
Figure 2. Raman spectrum of Sr_2CaWO_6 double perovskite recorded at ambient conditions. Only 17 (as indicated), from a total of 24 Raman active modes ($M = 12A_g + 12B_g$), are observed.

bronzes and oxides [8–14]. For example, in $KNbW_2O_9$, the two highest frequencies, centred at 900 and 960 cm^{-1}, were assigned to the W–O terminal bonds [9].

Raman spectra of Sr_2CaWO_6 were collected at room temperature and elevated pressures, up to 50.8 GPa; see figures 3 and 4.

The features of the changes shown by the bands can be summarized as follows: all the bands in the whole frequency region (100–1100 cm^{-1}) exhibit important frequency shifts (figure 5); the slopes of which are different from one frequency to another (table 1). All the bands change in height, in general smearing out as the pressure increases. There are some exceptions: for instance, when the pressure is increased from 3.2 to 9 GPa the intensity of some bands increases, and at 10.4 GPa it starts decreasing again. Finally, some bands appear, suddenly; some others merge; and some others split. This is the case, for example, of the band near 340 cm^{-1}. The number of observed modes decreases from 17 at 1 atm, to 13 at 14.5 GPa, to 9 at 19.7 GPa. At 37.6 GPa, only four modes are observed, and are present, also, at 50.8 GPa. All these features can be observed in three different pressure ranges: 1 atm to 3.2 GPa, 3.2–10.4 GPa and 10.4–50.8 GPa.

Let us now discuss the pressure dependence of the Raman spectra in the middle and low frequency ranges. The bands centred at 156.7 and 171.8 cm^{-1} overlap, at 12.2 GPa, leading to one broad band at high pressures. The shoulder observed around 200 cm^{-1}, at room pressure, becomes a resolved band at 5 GPa. The splitting is not due to a phase transition, but results from an overlapping of two bands attributed to the external modes of WO_6. The bands become separated at high pressures, owing to their different pressure dependences. As pressure increases, the shift of this band becomes very strong; and the band gets broad, and disappears at 24.6 GPa. The 339.2 cm^{-1} band starts getting broad as pressure reaches 3.2 GPa; and splits into two components when pressure reaches 6.8 GPa. This splitting increases with increasing pressure. The high wavenumber component exhibits a relatively strong pressure dependence. At first, when it appears, it achieves a higher intensity value than the low frequency wavenumber component. Then, it decreases in intensity until its complete
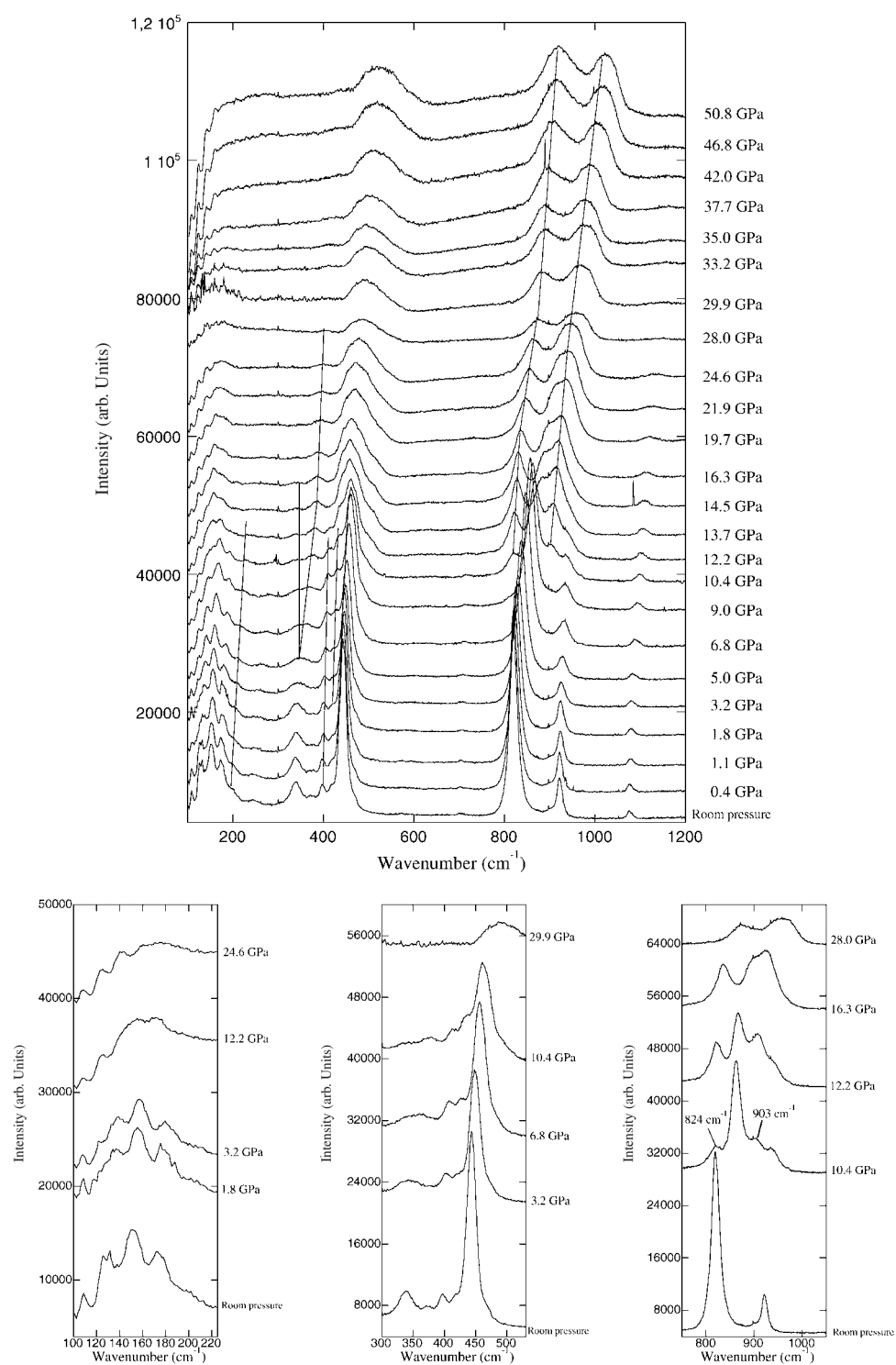
Figure 3. Raman spectra of Sr_2CaWO_6 recorded at room temperature and at increasing pressures, as indicated.
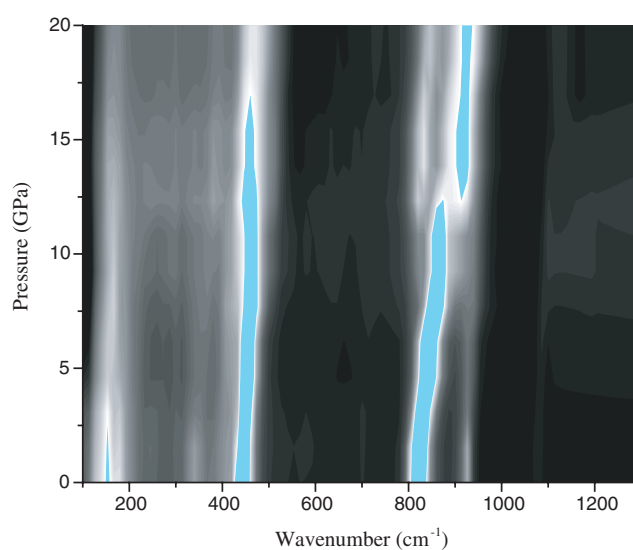
Figure 4. Section of the Raman spectra of Sr_2CaWO_6 recorded at room temperature and at increasing pressures. The section has been obtained cutting the spectra at two different intensity levels: to show, more clearly, the features of the changes in the bands. A grey scale colour code has been used: white colour stands for the highest intensity values, and the black colour for the lowest ones.

(This figure is in colour only in the electronic version)

Table 1. Raman band positions observed for Sr_2CaWO_6 at room conditions, frequency shifts with pressure and band assignments.

Frequency (cm^{-1})	df/dP (cm^{-1} GPa^{-1})	Assignment
129.0	1.56	
151.7	1.68	
173.0	1.86	Lattice modes
189.3	3.35	
245.0	3.99	
339.2	2.20	
372.9	1.62	W–O–W
396.8	1.62	Bending modes
419.0	1.45	
442.0	1.82	
571.1	—	
588.5	1.66	W–O
703.3	4.2	Stretching modes
819.6	—	
899.0	—	W–O
921.6	1.41	Stretching modes
1076.0	2.14	Overtone (921.6 cm^{-1} + 151.7 cm^{-1})

disappearance, at around 29.9 GPa. The low wavenumber component, with a lower intensity, is not so sensitive to pressure. It should be mentioned that these changes taking place in the 339.2 cm^{-1} band are also accompanied by a slope change of the frequency shift of the bands
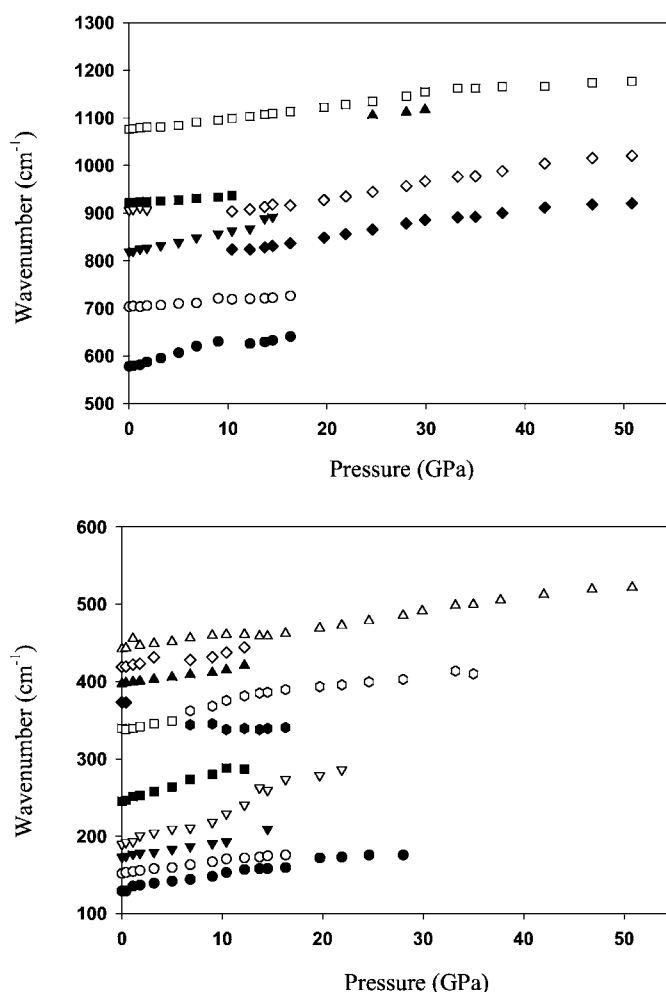
Figure 5. The pressure dependence of the observed Raman bands in Sr_2CaWO_6: (a) the low-frequency modes (100–550 cm^{-1}); and (b) the high-frequency modes (550–1200 cm^{-1}).

seen in the rest of the ranges. Therefore, we think that at 3.2 GPa a phase transition could occur. With increasing pressure, the left weak shoulder of the 442 cm^{-1} strong band gets stronger (starting at 3.2 GPa), until it becomes an independent band at around 6.8 GPa. At this pressure, both bands show strong pressure dependence. Therefore, this splitting cannot be explained by an overlapping of two bands: it may be a sign of a phase transition. This peak disappears when the phase transition at around 10.4 GPa occurs. The same remark stands for the independent band at 396.8 cm^{-1}: it has a constant intensity value, until it starts to disappear at 10.4 GPa. After the phase transition at 10.4 GPa, the bands observed at around 460 cm^{-1} become very broad at 12.2 GPa, as a result of the overlapping of bands. Upon further elevation of pressure, the bands observed at low frequencies decrease in intensity, giving rise to a small broad band, until it disappears at 35 GPa. The bands observed in the region 400–500 cm^{-1} overlap; and only one broad band is observed at and over 14.5 GPa. Because of the combined effect of a different shift rate of the bands and the decreasing of the intensity, the overlapping gets higher, and prevents a clear identification of the bands.
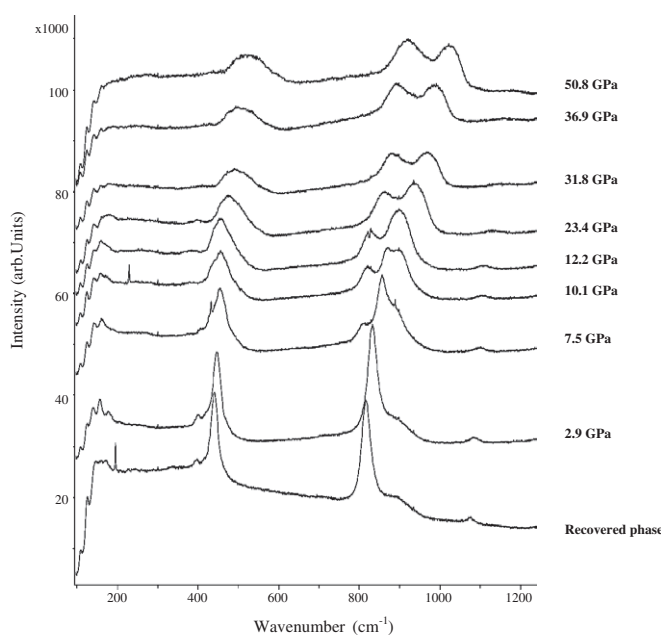
Figure 6. Raman spectra of Sr_2CaWO_6 double perovskite upon pressure release.

In the high-frequency range, upon elevation of pressure, Raman spectra show that up to 9.0 GPa all Sr_2CaWO_6 bands assigned to the $P2_1/n$ structure persist, with positive pressure shifts of the frequencies (see figure 5). Note that at 3.2 GPa there is a change in the shift slope, as mentioned previously. On the other hand, there are a number of discontinuities that develop in the spectra as the sample is compressed over 9.0 GPa. At 10.4 GPa, modes at 824 and 903 cm^{-1} come into existence, progressively increase in intensity, shift to the high frequencies and broaden. In the meanwhile, the bands at 863 and 937 cm^{-1} start decreasing in intensity. These two facts suggest that Sr_2CaWO_6 transforms to another structure. The transformation pressure, for Sr_2CaWO_6 at room temperature, is then given as $(9.0 + 10.4)/2 = 9.7 \pm 0.7$ GPa. As this new phase is compressed further, the intensity of the bands, especially those observed at 863 and 937 cm^{-1} (at 10.4 GPa), decreases significantly, until disappearance. Quite the contrary, peaks around 824 and 903 cm^{-1}, which are assigned to the W–O stretching modes, become stronger. They are strongly pressure dependent; they move almost parallel as a function of pressure (figure 5). The appearance of the two bands, probably, originates from the presence of two crystallographically distinct WO_6 units in the crystal: it seems that the new phase crystallizes with lower symmetry. It could also originate from different W–O distances. The modes at 824 and 903 cm^{-1} are lower in frequency than the bands at 863 and 937 cm^{-1}. Since those frequencies are related to the W–O distances, we may suggest that the new phase has larger W–O distances than those in the original phase.

Finally, the intense band from the room-pressure spectrum, centred at 820 cm^{-1}, merges with the one appearing at 903 cm^{-1}; afterwards, it decreases in intensity, until it completely disappears. When pressure increases, the 921.6 cm^{-1} mode, assigned to the W–O stretching vibration, clearly changes its height at 3.2 GPa, but it does not shift too much, showing that the band is short and strong. At 10.4 GPa this band starts merging with the new band which has appeared at 903 cm^{-1}; at 16.3 GPa it completely becomes part of the single band observed around 900 cm^{-1}. The sum of the frequencies of the two bands centred at 151.7 and 921.6 cm^{-1}
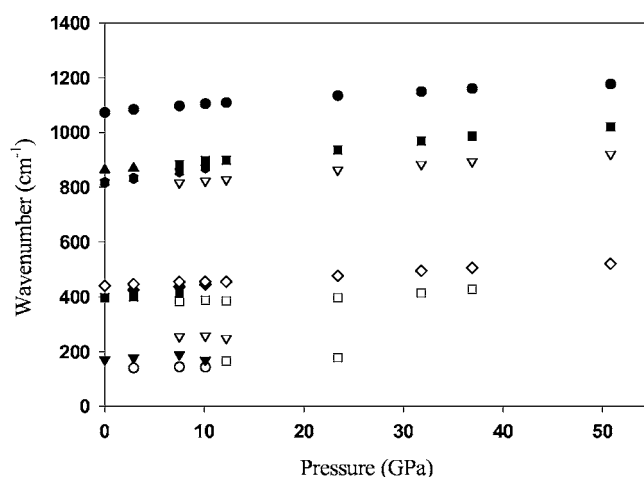
Figure 7. Pressure dependence of the observed Raman frequencies in Sr_2CaWO_6, upon pressure release.

(1 atm) matches the frequency of the highest band centred at $1076\,cm^{-1}$ (1 atm), over the 1 atm to 10.4 GPa pressure range. Therefore, this band is, probably, due to an overtone of the bands centred at 151.7 and $921.6\,cm^{-1}$ (1 atm).

The vibrational modes of the Sr_2CaWO_6 (high pressure structure) are measured up to 50.8 GPa and on decompression. Figure 6 shows the plot of the Raman spectra on decompression. Pressure shifts of these modes are plotted in figure 7. As illustrated in figure 6, the frequencies of the vibrations decrease continuously on decompression; 17 modes are observed at 1 atm in Sr_2CaWO_6 with $P2_1/n$, in comparison with the ten modes that are observed in the recovered phase over the same spectral region.

4. Conclusions

An *in situ* Raman spectroscopic study was conducted to explore the pressure-induced phase transformation of Sr_2CaWO_6 up to pressures of 50.8 GPa. Results indicate that structural changes are observed at 3.2 GPa, which is a possible phase transition. As the material is compressed further, there are a number of discontinuities that develop in the spectra: at 10.4 GPa, modes at 824 and $903\,cm^{-1}$ come into existence, suggesting strongly that Sr_2CaWO_6 undergoes a phase transition. Upon release of pressure to ambient conditions, ten modes are observed at 1 atm in the recovered phase of Sr_2CaWO_6, in comparison with 17 modes in the starting material with $P2_1/n$ structure that are observed over the same spectral region.

Acknowledgments

References

[1] Kobayashi K-I, Kimura T, Sawada H, Terakura K and Tokura Y 1998 *Nature* **395** 677–80
[2] DeMarco M, Blackstead H A, Dow J D, Wu M K, Chen D Y, Chien F Z, Haka M, Toorongian S and
       Fridmann J 2000 *Phys. Rev.* B **62** 14301–3
[3] Gateshki M and Igartua J M 2004 *J. Phys.: Condens. Matter* **16** 6639–49
[4] Liegeois-Duyckaerts M and Tarte P 1974 *Spectrochim. Acta* B **30** 1771–89
[5] Baldinozzi G, Sciau Ph and Bulou A 1995 *J. Phys.: Condens. Matter* **7** 8109–17
[6] Mao H K, Xu J and Bell P M 1986 *J. Geophys. Res.* A **191** 4673
[7] Kroumova E, Aroyo M I, Perez-Mato J M, Kirov A, Capillas C, Ivantchev S and Wondratschek H 2003 *Phase
       Transit.* **76** 155–70 (http://www.cryst.ehu.es)
[8] Daniel M F, Desbat B, Lassegues J C, Gerand B and Figlarz M 1987 *J. Solid State Chem.* **67** 235
[9] Maczka M, Hanuza J and Majchrowski A 2001 *J. Raman Spectrosc.* B **32** 929–36
[10] Kuzmin A, Purans J, Cazzanelli E, Vinegoni C and Mariotto G 1998 *J. Appl. Phys.* **84** 5515
[11] Oi J, Kishimoto A and Kudo T 1993 *J. Solid State Chem.* **103** 76
[12] Souza Filho A G, Freire P T C, Mendes Filho J, Kojima S, Hanuza J and Majchrowski A 2003 *Z. Anorg. Allg.
       Chem.* **131** 582
[13] Maczka M, Souza Filho A G, Freire P T C, Mendes Filho J, Kojima S, Hanuza J and Majchrowski A 2003
       J. Raman Spectrosc. **34** 199–204
[14] Maczka M, Hanuza J, Kojima S, Majchrowski A and van der Maas J H 2001 *J. Raman Spectrosc.* **32** 287–91